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t-BUTYLDIMETHYLSILYL DERIVATIVES OF SOME ALKYLPHOSPHONIC AND ALKYL METHYLPHOSPHONIC ACIDS. PART I. GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC STUDIES

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ABSTRACT

Electron impact mass spectra have been generated for t-butyldimethylsilyl derivatives of several alkyl methylphosphonic, alkylphosphonic and halogen-substituted alkylphosphonic acids. In all cases, fragmentation is limited to a few abundant ions indicating that improved quantitation of this class of compounds, essential for verification of chemical arms agreements, will be possible by gas chromatographic/mass spectrometric means using these derivatives. Some fragmentation mechanisms are suggested to account for the major ions of the spectra.

RÉSUMÉ

On a obtenu avec une source à impact électronique le spectre de masse des dérivés t-butyldiméthylsilyl de plusieurs acides alkyl méthylphosphoniques, alkylphosphoniques et alkylphosphoniques halogénés. Dans tous les cas, la fragmentation est limitée à quelques ions abondants, indiquant ainsi qu'il sera possible de mettre au point de meilleures méthodes de dosage des acides organophosphoniques utilisant la chromatographie en phase gazeuse/spectrométrie de masse de ces dérivés; de telles méthodes sont essentielles à la vérification des accords sur les armes chimiques. On propose certains mécanismes de fragmentation pour rendre compte des ions principaux sur les spectres.

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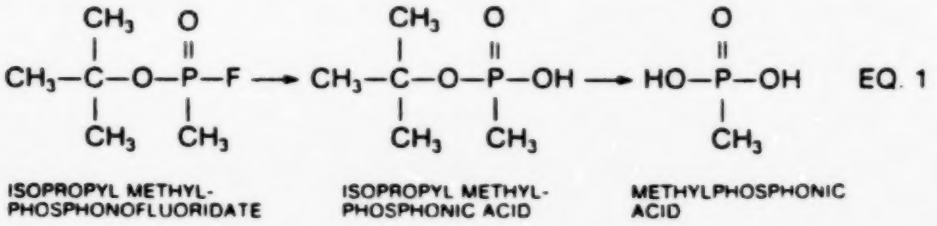
1.0 INTRODUCTION

In the negotiations at the Committee on Disarmament in Geneva for a total ban on the development, production and stockpiling of chemical weapons [1], some provisions may require procedures for the identification and verification of the presence of chemical warfare agents, their precursors and by-products of production. In the case of organophosphorus nerve agents, detection and quantitation by gas chromatography (GC) in the nanogram-to-picogram ranges is reasonably straightforward after extraction from water, vegetation, etc. has been achieved [1-9]. In addition, gas chromatography/mass spectrometry (GC/MS) can provide unequivocal identification of these compounds [7-10]. Nerve agents however, are unstable in water, hydrolyzing to produce alkylphosphonic acids [3,9,11-13]. For example, isopropyl methylphosphonofluoridate (Sarin) may be expected to hydrolyse as follows [3,9,11-13] (Eq. 1):



EQ. 1

In similar manner, pinacolyl methylphosphonofluoridate (Soman) and O-ethyl S-2-diisopropylaminoethyl methylphosphonothioate (VX) would be

expected to yield among other products, pinacolyl methylphosphonic acid and ethyl methylphosphonic acid respectively, and ultimately, methylphosphonic acid [3,12,13].

Unfortunately the alkylphosphonic acids are more difficult to analyze as they possess low volatility, are polar and, as such, are not readily amenable to direct GC or GC/MS quantitation or identification. A similar situation exists for many organophosphorus pesticides which primarily form alkylphosphoric acids on hydrolysis [12b]. The popular procedure for analyzing alkylphosphonic and alkylphosphoric acids involves methylation with diazomethane to form methyl esters which are often readily analyzed by GC or GC/MS [3-4, 12-14]. Although extensively used, diazoalkylation has disadvantages in that the reagents used are toxic and generation of diazomethane can be explosive and, in some cases, methylation can be incomplete [12a,13,14c].

Trimethylsilylation of phosphorus acids and anions has been used for gas chromatographic and GC/MS analyses [15]. Bauer and Vogt employed N,O-bis(trimethysilyl)trifluoroacetamide (BSTFA) at room temperature to effect derivatization of phosphorus acids, however they noted that the BSTFA and silylation products exhibited high hydrolytic sensitivity necessitating careful manipulation of the solutions [15g]. Griest and Martin observed that both the trimethylsilyl and methyl derivatives of dibutylphosphate exhibited tailing necessitating the development of a different procedure in which the dibutylphosphate is converted to dibutylphosphorofluoridate [16]. As they note, however; some of the fluorophosphorus compounds can be very toxic [16]. Other workers have

effected trimethylsilylation using heated pre-column or on-column derivatization of phosphate anions [17].

In their investigation of the analysis of alkylphosphonic acids the Finnish investigators, who were unsatisfied with diazomethane methylation due to capillary column deterioration, incomplete conversion necessitating sample clean-up, short retention times, and a general lack of high mass ions for favorable mass spectrometric selected ion monitoring, commenced the development of a different derivatization procedure [9,13]. It was anticipated that pentafluorobenzyl (PFB) derivatives would offer advantages for electron-capture GC, UV-HPLC and negative ion-mass spectrometric detection. However, it was found that the formation reaction is slow even when 18-Crown-6 is added to improve reactivity [13]. Subsequently, they reported that the PFB derivatization of alkylphosphonic acids is best carried out using a large excess of PFB-Br with sodium hydride and 18-Crown-6 in THF at 45°C for five hours [9].

One liquid chromatographic method for phosphinic and phosphonic acid analysis oxidizes the compounds in a post-separation-column reactor for subsequent UV detection of a colored compound resulting from the reaction of acidic molybdenum (V) and (VI) with the orthophosphate [18]. In another study of liquid chromatographic analysis, alkyl methylphosphonic acids were derivatized with p-bromophenacyl bromide in the presence of potassium carbonate and 18-Crown-6 to form the esters which were cleanly separated for UV quantitation [19]. Detection limits were given as 40-60 ng for alkyl methylphosphonic acids.

For the analysis of alkylphosphonic acids by both GC and GC/MS, a new derivatization procedure is required which combines the attributes of simplicity, speed, safety, stability, detection sensitivity and clean GC separation. The t-butyldimethylsilyl group has been used as a protecting group in the synthesis of compounds such as prostaglandins and deoxynucleosides [20] as well as a derivative for GC, GC/MS and MS analysis of a number of compounds [20b,21]. In many of these cases, hydroxyl groups are being derivatized, but carboxylic and phosphoric acids have also been successfully converted [21b,j,k]. In the case of phosphorus acids, derivatization resulted in single sharp symmetrical GC peaks [21k]. The derivatives are easily made and are stable for over a week at room temperature and for six months at 4°C [21k]. More importantly, the mass spectra are dominated by $[M-57]^+$ base peaks, the loss of a t-butyl group [21k]. We report here the mass spectra of t-butyldimethylsilyl derivatives of several alkylphosphonic mono- and diacids. Details of stabilities, optimum reaction conditions and detection limits for FPD-GC and GC/MS of these promising derivatives will be reported elsewhere [22].

2.0 EXPERIMENTAL

2.1 Reagents and Instruments

N-methyl-N-(t-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) was obtained from Regis Chemical Company (Morton Grove Ill, U.S.A.). Silylation grade acetonitrile and toluene were obtained from Pierce Chemical Company (Rockford, Ill, U.S.A.). The phosphonic acids for

preparation of compounds 4-8 were purchased from Fairfield Chemical Company (Blythewood, S.C., U.S.A.) while those for preparation of compounds 1 and 2 were provided by courtesy of Dr. E.W. Sarver, Chemical Research and Development Center, Aberdeen Proving Ground, Maryland, 21010, USA. Pinacolyl methylphosphonic acid for preparation of compound 3 was prepared at DREO by controlled hydrolysis of the corresponding phosphonofluoridate.

GC/MS analyses were performed on a Finnigan 4023 gas chromatograph/quadrupole mass spectrometer equipped with a fused silica capillary column (30m x 0.258mm I.D) DB5-30N (J & W Scientific Inc.).

All volumetric measurements were carried out using Hamilton syringes. Samples were prepared and stored in screw cap glass vials with Teflon/silicone septa (Pierce Chemical Company). All derivatizations were performed in a Pierce Reacti-Therm Heating/Stirring Module.

2.2 Derivatization Procedure

A typical derivatization involved combining 20 µL of a stock solution of the phosphonic acid (5 µg/µL) in acetonitrile with 80 µl of acetonitrile, 200 µL of MTBSTFA, and 200 µL of toluene. The mixture was then heated to 60°C for 1 hour with stirring in a sealed Reacti-vial followed by Grob injection into the GC/MS for analysis.

2.3 Instrumental Parameters

For GC/MS analysis the conditions were: carrier gas, helium; flow-rate, 1.11 mL/min; injector temperature, 230°C; source temperature, 190°C; ionization mode, electron impact at 70 ev; GC column temperature program (for most samples), 50°C for 1.6 minutes (slow injection at 0.8 minutes, split at 1.7 minutes), 50°C to 140°C at 22°/minute followed by increase to 200°C at 5°/minute and hold; (for compound **8**), as above but 50°C to 100°C at 4°/minute and 100°C to 250°C at 10°/minute and hold.

3.0 RESULTS AND DISCUSSION

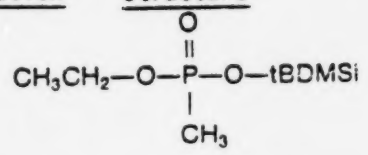
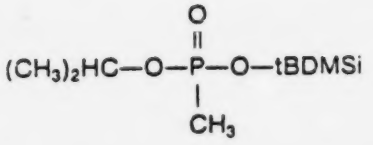
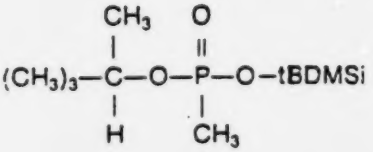
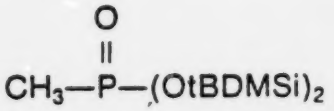
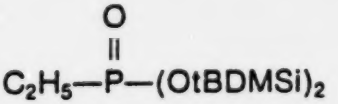
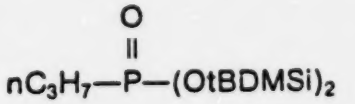
Electron impact mass spectra have been generated for the t-butyldimethylsilyl derivatives of several alkyl methylphosphonic, alkylphosphonic and chlorine-substituted alkylphosphonic acids (Table 1). The main features (rel.ab. > 5%) of the mass spectra of these compounds are given in Table 2 and the mass spectra are included in the Appendix. The spectra will be discussed under the three separate groups of compounds, the alkyl methylphosphonic acid derivatives, the alkylphosphonic acid derivatives and derivatized chloroethylphosphonic acid.

3.1 Alkyl Methylphosphonic Acid Derivatives (Compounds 1-3)

In general, the mass spectra of the derivatized alkyl methylphosphonic acids exhibit little or no parent molecular ion, a

TABLE 1

COMPOUNDS INVESTIGATED

Sample Identification[a]	Structure	Systematic Name
1		t-Butyldimethysilylethyl methylphosphonate
2		t-Butyldimethylsilyliso-propyl methylphosphonate
3		t-Butyldimethylsilylpinacolyl methylphosphonate
4		Bis(t-Butyldimethylsilyl) methylphosphonate
5		Bis(t-Butyldimethylsilyl) ethylphosphonate
6		Bis(t-Butyldimethylsilyl) n-propylphosphonate

Sample Identification[a]	Structure	Systematic Name
7	$nC_4H_9—P(=O)—(OtBDMSi)_2$	Bis(t-Butyldimethylsilyl) n-butylphosphonate
8	$ClCH_2CH_2—P(=O)—(OtBDMSi)_2$	Bis(t-Butyldimethylsilyl) 2-chloroethylphosphonate [Bis(t-Butyldimethylsilyl) derivative of Ethephon]

[a] Numbers used in text to identify each compound.

characteristic commonly observed for mass spectra of phosphonate esters [10]. There is, however, some occurence of loss of 15u or CH_3 which probably originates from the dimethylsilyl grouping [23]. The mass spectra of the derivatives 1-3 examined in this study are dominated by the same base peak occuring at m/z 153 and accounting for 38, 41 and 32% of the total ion count respectively. In general, three ions predominate in the spectra, totalling 63, 54 and 41% of the total ion current for compounds 1-3 respectively. As anticipated, increases in the size and complexity of the alkyl group present additional pathways for fragmentation and overall fragmentation therefore increases. The major ions found are the base peak at m/z 153, an ion at m/z 75 and an ion occuring at the m/z (M-57) where M is the molecular species.

TABLE 2

[a]Principal Ions in the Mass Spectra of t-Butyldimethylsilyl Alkyl Phosphonates 1-8

m/z(relative abundance, %)

	1	2	3	4	5	6	7	8
$(M)^{+\cdot}$	238(⟶)	252(⟶)	266(⟶)	324(<0.1)	338(<0.1)	352(<0.1)	366(0.2)	372(⟶)
$(M-CH_3)^+$	223(0.9)	237(2.7)	279(0.4)	309(3.6)	323(4.1)	337(3.2)	351(3.7)	357(2.1)
$(M-C_4H_8)^{+\cdot}$	182(5.4)	[c]196(1.0)	238(1.7)	268(19.3)	282(24.9)	296(22.1)	310(24.1)	316(19.6
$(M-C_4H_9)^+$	[c]181(36.5)	[c]195(7.7)	237(6.9)	267(100.0)	281(100.0)	295(100.0)	309(100.0)	315(100.0)
$(M-CH_3-C_4H_8)^+$	167(0.2)	181(⟶)	223(⟶)	253(0.3)	267(4.4)	281(5.6)	295(3.5)	301(⟶)
[b]$(M-C_4H_9-R')^+$	153(100.0)	153(100.0)	153(100.0)	153(12.0)	167(11.8)	[c]181(13.4)	[c]195(17.4)	201(1.3)
$(M-C_4H_9-CH_2C(CH_3)_2)^{+\cdot}$	126(⟶)	140(⟶)	182(5.9)	212(6.1)	226(7.4)	240(4.1)	254(1.8)	260(0.8)
$[C_4H_{13}O_3PSi_2]^{+\cdot}$?	196(0.2)	[c]196(1.0)	196(0.2)	196(2.5)	196(10.8)	196(10.0)	196(7.1)	196(8.4)
$[C_4H_{12}O_3PSi_2]^+$?	195(1.3)	[c]195(7.7)	195(2.7)	195(7.2)	195(13.9)	195(15.4)	[c]195(17.4)	195(16.8)
$[HOP(O)OH_2OSi(CH_3)_2H]^{+\cdot}$?	154(8.1)	154(10.3)	154(10.3)	154(1.1)	154(0.1)	154(0.1)	154(<0.1)	154(⟶)
$[(CH_3)_2Si=OSi(CH_3)_3]^+$	147(⟶)	147(⟶)	147(0.7)	147(3.9)	147(8.5)	147(11.2)	147(8.5)	147(3.9)
?	135(0.1)	135(⟶)	135(0.2)	135(13.0)	135(18.1)	135(21.0)	135(14.7)	135(17.3)
$[(CH_3)_2Si=O-Si(CH_3)_2H]^+$?	133(⟶)	133(⟶)	133(0.2)	133(7.4)	133(11.5)	133(13.5)	133(9.5)	133(14.3)
?	123(5.2)	123(3.7)	123(2.4)	123(0.6)	123(1.1)	123(1.3)	123(0.9)	123(1.1)
$[C_2H_6O_2PSi]^+$?	121(7.0)	121(7.1)	121(9.1)	121(2.3)	121(4.8)	121(6.2)	121(4.7)	121(4.1)
$[HOP(O)OH_2OSi(CH_3)_2H]^{++}$?	77(5.6)	77(6.5)	77(4.8)	77(1.4)	77(1.8)	77(2.0)	77(1.3)	77(2.1)
$[(CH_3)_2Si=OH]^+$	75(28.4)	75(24.2)	75(19.7)	75(4.6)	75(7.6)	75(8.4)	75(5.7)	75(5.6)
$[(CH_3)_3Si]^+$	73(6.2)	73(7.7)	73(13.2)	73(28.0)	73(48.5)	73(59.5)	73(42.8)	73(42.3)
$[Si(CH_3)_2H]^+$?	59(2.8)	59(3.5)	59(3.0)	59(3.7)	59(6.6)	59(7.6)	59(5.3)	59(5.5)
$[Si(CH_3)_2]^{+\cdot}$?	58(0.7)	58(0.7)	58(1.0)	58(0.9)	58(1.5)	58(1.7)	58(1.3)	58(2.3)
$[C_4H_9]^+$	57(2.8)	57(3.5)	57(9.1)	57(3.5)	57(6.9)	57(9.5)	57(7.8)	57(34.7)
$[Si(CH_3)H_2]^+$?	45(4.8)	45(5.0)	45(3.5)	45(2.4)	45(3.6)	45(3.9)	45(2.4)	45(3.0)
MISCELLANEOUS								
	210(⟶)	210(⟶)	210(0.1)	210(3.6)	210(1.2)	210(2.7)	210(5.1)	210(⟶)
	[c]181(36.5)	181(⟶)	181(0.3)	181(1.5)	181(5.3)	[c]181(13.4)	181(3.9)	191(2.1)
	69(0.2)	69(⟶)	69(8.5)	69(⟶)	69(0.2)	69(0.2)	69(0.2)	69(⟶)
	55(0.8)	55(0.8)	55(5.0)	55(0.6)	55(1.1)	55(1.3)	55(2.5)	55(1.3)
		43(5.7)	43(12.9)	43(1.1)				
		41(11.9)	41(26.5)	41(5.0)				
		39(2.9)	39(7.8)	39(1.5)				
								289(9.6)
								287(24.9)
								247(9.5)
								246(3.3)
								245(24.8)
								230(2.4)
								217(2.4)
								215(1.1)
								213(6.2)
								169(3.2)
								167(9.0)
								99(2.3)
								93(6.4)
Base Peak as % Σ	Σ_{45}(38.2)	Σ_{37}(40.8)	Σ_{37}(32.1)	Σ_{36}(34.6)	Σ_{45}(25.6)	Σ_{45}(23.4)	Σ_{45}(27.8)	Σ_{45}(18.9)

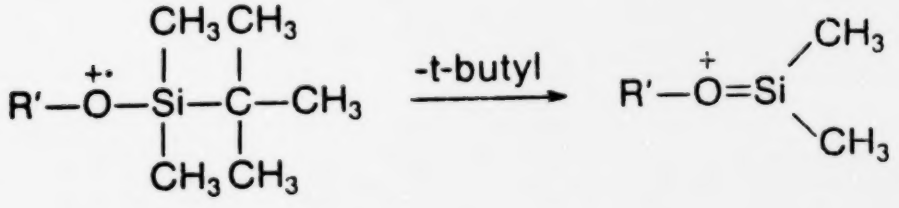
FOOTNOTES

a Intensities not corrected for natural abundance of neighbouring fragment ions.

b For compounds 1-5, R' represents the unsaturated radical related to the alkyl group attached to the phosphorus atom through oxygen. For compounds 6-8, R' represents the t-butyldimethylsilyl group after transfer of one hydrogen to the ion fragment.

c Indicates duplicate entry occurring as a specific m/z as well as suggested fragment loss $[M-R-Y]^{+\cdot}$

The $[M-57]^+$ ion is formed by the loss of a t-butyl radical from the silyl group of the parent ion. This process is typical of that observed in a number of mass spectral investigations of t-BDMS derivatives (see [21] for example) and has been interpreted as the formation of a double-bonded silicon-oxygen moiety (Scheme 1) [21c]. In contrast to some systems, the abundance of the $[M-57]^+$ ion in the alkyl

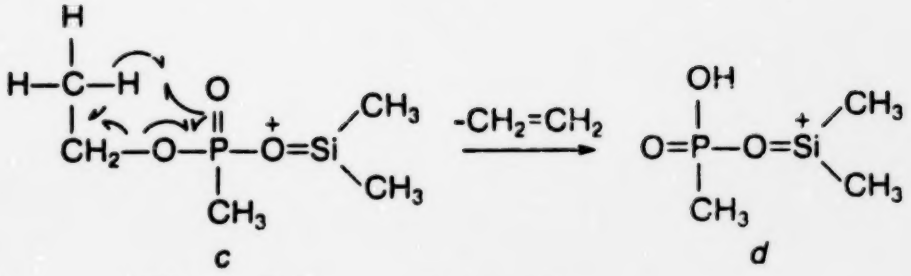


a *b*

Scheme 1

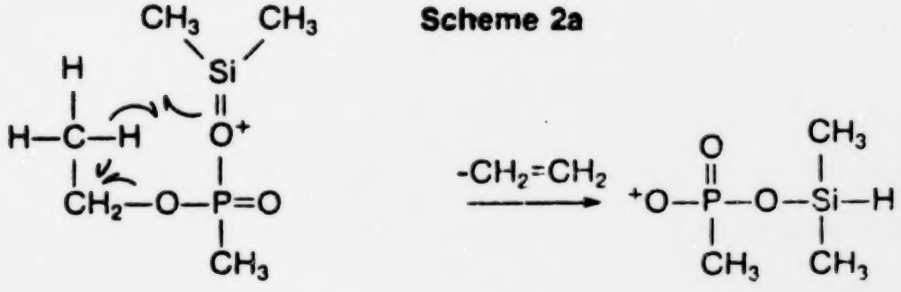
methylphosphonic acid derivatives is significantly less than that for the base peak.

The base peak occuring at m/z 153 can be attributed to a further rearrangement and dissociation of the $[M-57]^+$ ion; namely, a hydrogen transfer from the alkyl group followed by olefin elimination. The transfer of the hydrogen can occur however, as depicted in Schemes 2a or 2b for compound 1. Although the stability for the species in Scheme 2a may be greater, the presence of a significant abundance at m/z 59 suggests the existence of a precursor for the ion $[Si(CH_3)_2H]^+$.



c *d*

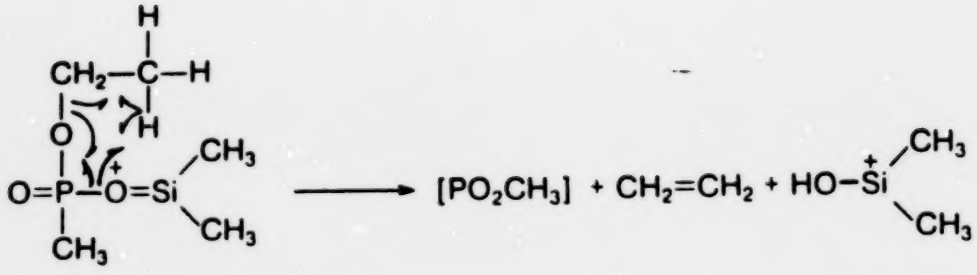
Scheme 2a



c *e*

Scheme 2b

The peak at m/z 75, dominant in the mass spectra of the t-BDMS-derivatized alkyl methylphosphonic acids, is also significant in the alkyl- and halogen-substituted alkylphosphonic acid derivatives. It has been observed in the t-BDMS derivatives of prostaglandins [21a] steroids [21c], the trimethylsilyl (TMS)-ether derivatives of alcohols [23a], the TMS derivatives of w-Phenoxyalkanoic acids [23b], the t-BDMS derivatives of inorganic oxyanions [21k], and other silyl ethers [15d,21b,f,h, 24-28]. It is now accepted that the species is dimethylsilanol $[(CH_3)_2Si - OH]^+$. In the compounds under study in this investigation, subsequent dissociation of the abundant $[M-57]^+$ ion to produce the m/z 75 ion is possible by way of a hydrogen-transfer rearrangement as depicted for compound 1 (Scheme 3).

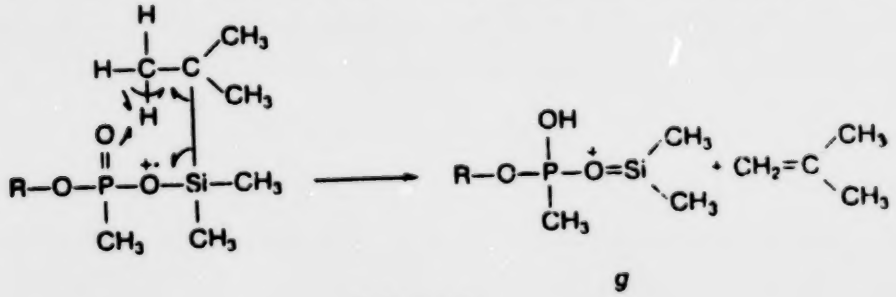


c *f*

Scheme 3

Dissociation and rearrangement of the ion of Scheme 2b would result in the same observations.

Although it is not a major ion, the species at (M-56) is worthy of comment as it may be the precursor to other ions. Close examination of the relative abundance of the $[M-56]^+$ ion to that of the $[M-57]^+$ ion indicates that the relative intensity cannot be accounted for on the basis of natural isotopic abundance of the $[M-57]^+$ ion. The $[M-56]^+$ species may be the result of a rearrangement involving hydrogen transfer from the t-butyl group and olefin elimination as depicted in Scheme 4.



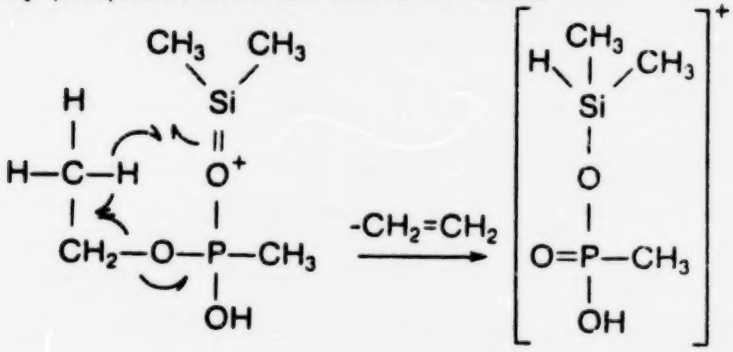
g

Scheme 4

In the case of compound 1, the ion at m/z 123 amounts to 5% relative intensity and considerably less for compounds 2 and 3. Cleavage of the silicon-oxygen bond is one possible mechanism by which an ion at this m/z could be produced. The peak at m/z 121 is found in the spectra of all compounds studied in this investigation although it is more abundant in the derivatized alkyl methylphosphonic acids. The calculated isotope ratio of m/z 122/121 based on the compound formula $C_2H_6O_2PSi$ is 7.5 while for compounds 1-7, the ratios 10.7, 6.5, 8.2, 8.8, 8.7, 8.5 and 8.5 are observed. An alternative formula $C_3H_{10}POSi$ has a calculated isotope ratio of 8.6 which is in better agreement; however, the presence of only one oxygen would be difficult to account for in a reasonable Scheme. Until the elemental formula is verified, further speculation concerning the structure of the ion and a mechanism for its formation must be deferred. High resolution work is now underway to resolve the elemental formula of this and several other ions.

The relative abundances of the ion at m/z 77 are significant for the derivatized alkyl methylphosphonic acids, ranging from 4.8-6.5% but are 2% or less for the alkylphosphonic acid derivatives. It is difficult to propose a reasonable combination of elements to account for an ion at m/z 77. It seems more likely that it is the doubly charged species of m/z 154. The relative abundance of m/z 154 in compounds 2 and 3, at least, is greater than that predicted for the natural abundance of the proposed species at m/z 153. One proposal for the structure of the m/z 154 ion involves a hydrogen transfer with olefin elimination in the $[M-56]^+$ ion. As discussed above, the possibility of a source additional

to the natural abundance of the $[M-57]^+$ ion is indicated by the ratio of relative abundances of (m+1)/(m) for m/z $[M-57]^+$. The ion *g* shown in Scheme 4 could undergo a further hydrogen transfer and olefin elimination involving the alkyl group as shown for the ethyl methylphosphonic acid derivative in Scheme 5.



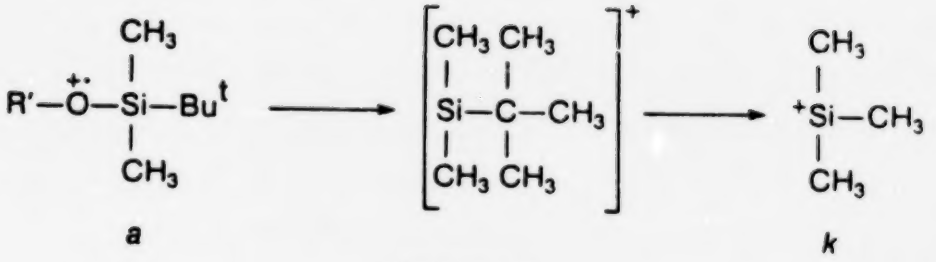
h *i*

Scheme 5

A subsequent pathway for dissociation of the ion at m/z 154 would be cleavage of the silicon-oxygen bond to yield an ion at m/z 59. In fact, the relative abundances for m/z 59 range from 2.8-3.5% for the alkyl methylphosphonic acid derivatives and from 3.7 to 7.6 for the alkylphosphonic acid derivatives. Cleavage of the phosphorus-oxygen bond would result in an ion at m/z 75 or an isomer of dimethylsilanol.

The abundant ion at m/z 73 is considered to be due to the fragment $[(CH_3)_3Si]^+$. Normally found in trimethylsilyl (TMS) derivatives [15b,d,21a,i,23-25,28,29], its presence in the spectra of t-BDMS derivatives has been noted previously [21b,c,h,k,26] and its origin has been shown to be a rearrangement of the t-butyl group attached to the

silicon atom [26] (Scheme 6).



Scheme 6

For the alkyl methylphosphonic acid derivatives, the peaks at m/z 115 are of low abundance (0.2, 0.03 and 0.13%), a behaviour similar to that observed for t-butyldimethylethoxysilane [26].

Finally, significant response (rel. ab. 3.5-5.0%) is recorded for the ion at m/z 45. The relatively high ratio of abundances of m/z 46 and 45 indicate that silicon may be present suggesting a species with elemental formula of $[SiH_2CH_3]^+$ [15b] which would result from successive hydrogen transfer, one step of which might resemble the process suggested in Scheme 2b.

3.2 Alkylphosphonic Acid Derivatives (Compounds 4-7)

In contrast to the derivatives of alkyl methylphosphonic acids, all of the alkylphosphonic acid derivatives studied in this investigation have as their base peak the ion resulting from a loss of the t-butyl group $[M-57]^+$. The abundance of the ion corresponding to the base peak of the derivatized alkyl methylphosphonic acids ($M-C_4H_9-R'$), although still significant, only exhibits relative abundances of 11-13%. Like the

alkyl methylphosphonate derivatives, the molecular ion abundance is either very low or zero although there is some occurrence of loss of methyl radicals (M-15). There are other differences in the cracking patterns of these two classes of derivatives as well. Peaks at m/z 196, 195, 147, 135, 133, 73, 59 and 57 now have significant abundances as compared to the spectra of the alkyl methylphosphonic acid derivatives whereas the relative importance of m/z (M-57-R'), 77 and 75 has decreased. Again, a large proportion of the ion current resides in a small number of ions, e.g. the percentage of total ion current contributed by the four ions at m/z (M-57), 195, 135, and 73 is 51, 46, 46 and 49% for compounds 4-7 respectively.

In the derivatized alkylphosphonic acids, the ion at m/z 195 is abundant with up to 15% relative intensity. Since it does not consistently possess high abundance (unless fortuitously being a prominent ion such as $[M-57]^+$ in compound 2) in the alkyl methylphosphonic acid derivatives, the influence of a second silicon group is indicated. The significant abundance at m/z 196 is consistent with the presence of both silicon atoms although, as will be discussed later, other sources for the ion at m/z 196 are possible. Since the ion at m/z 195 is observed in all derivatized alkylphosphonic acids and even in the 2-chloroethylphosphonic acid derivative, it is apparent that the alkyl group, at least, is not retained. One elemental formula which is consistent with these observations is $C_4H_{12}O_3PSi_2$ suggesting that both t-butyl groups have been lost and that the alkyl group has been cleaved from the phosphorus. In general, the ratio of the abundances of the ions at m/z 196 to m/z 195 is much greater than is required for the natural

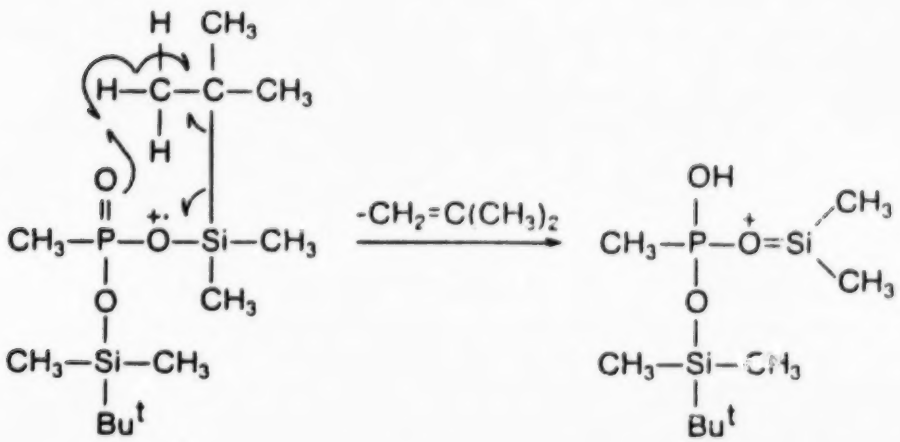
abundance of m/z 195 even with two silicon atoms. If it is assumed that the ion at m/z 195 involves the loss of the two t-butyl and the alkyl groups, the ion at m/z 196 could involve a hydrogen transfer and elimination of isobutene from one silicon atom coupled with the loss of the second t-butyl group and the alkyl group. High resolution mass spectra are being generated to verify the formula before attempting further examination of these ions.

Another ion which exhibits similar characteristics is observed at m/z 135. The high abundance for the derivatized alkylphosphonic acids but negligible levels in the derivatized alkyl methylphosphonic acids indicates that it, too, results from the disilyl nature of compounds **4-8**. Its consistently abundant presence in all of these compounds implies that the alkyl group has been expelled although any proposal for the structure of this ion, like that of m/z 195 and m/z 196, must await formula verification.

A number of other features and differences between the spectra of this class of compounds and the derivatized alkyl methylphosphonic acids deserve mention. For instance, the abundance of the $[M-56]^+$ ion in the alkylphosphonic acid derivatives exceeds that expected from the natural abundance of the $[M-57]^+$ ion, like the situation for the alkyl methylphosphonic acid derivatives. As pointed out above, the relative abundance of the ion at $[M-C_4H_9-R']^+$ where R' is the t-BDMS group after one hydrogen transfer is considerably less than is found for the alkyl methylphosphonic acid derivatives where R' is the unsaturated radical derived from the alkyl group on the oxygen atom. One of the probable

reasons for this observation is the lack of an alkyl group in the alkylphosphonic acid derivatives which can readily transfer a hydrogen atom and undergo olefin elimination as depicted in Schemes 2a,b. Nevertheless a mechanism for its formation in the alkylphosphonic acid derivatives is required. A variation of Scheme 2a involving the elimination of the isobutene group is one possible pathway as depicted for compound **4** in Scheme 7. Ion *l* would then be required to undergo a silicon-oxygen bond cleavage to produce the ion *m*.

A reaction analogous to Scheme 2b is unlikely since elimination of

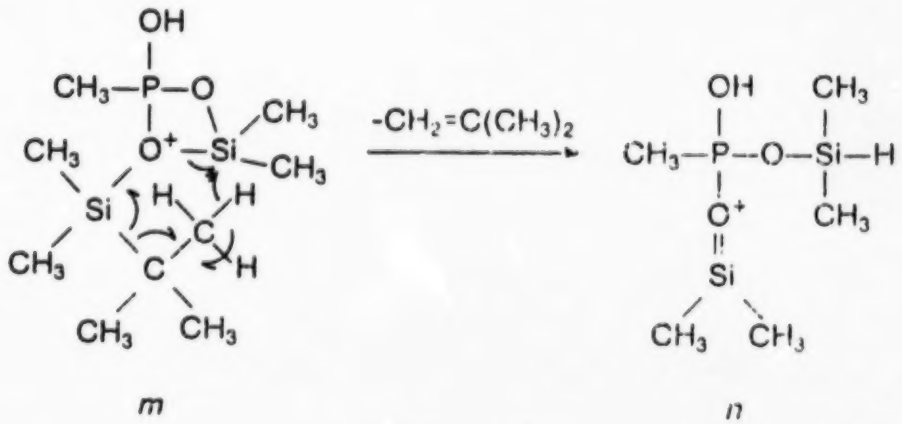


l *m*

Scheme 7

isobutene with hydrogen transfer would need to be followed by cleavage of the resulting silicon-oxygen double bond. The first step, elimination of isobutene with hydrogen transfer, may be occurring however. The loss of 112 u from the molecular ion yields an ion with relative abundance ranging from 7.4% for compound **5** to 2% for compound **7**. One

possible representation of ion *m* involves a cyclic structure similar to others which have been proposed for trimethylsilyl derivatives [27,30]. Further hydrogen transfer and olefin elimination involving the second t-butyl group would yield the $[M-112]^+$ ion as depicted for compound **4** in Scheme 8. The abundance of an ion at m/z 59 which



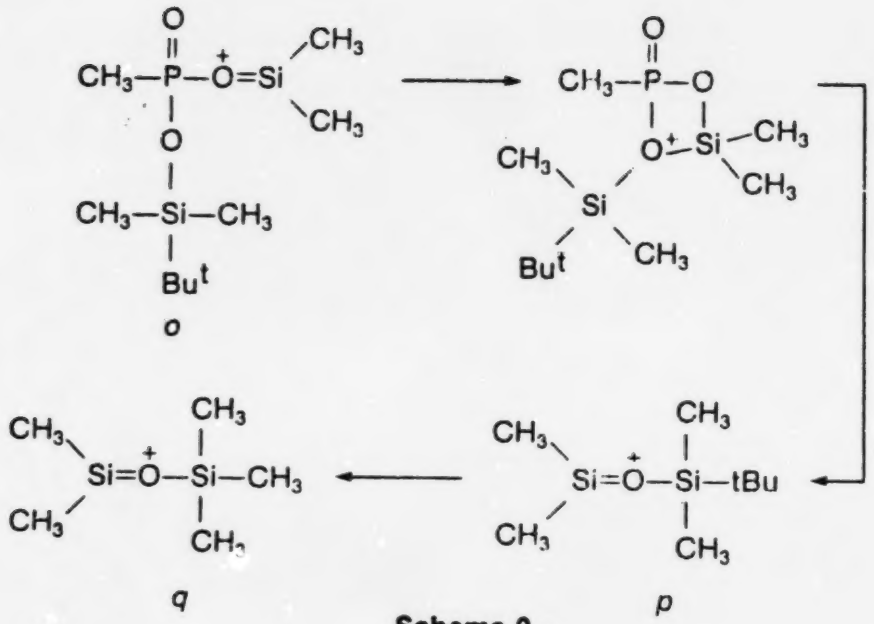
m *n*

Scheme 8

could result from further cleavage of the single silicon-oxygen bond to yield $[SiH(CH_3)_2]^+$ lends further support for the existence of ion *n*.

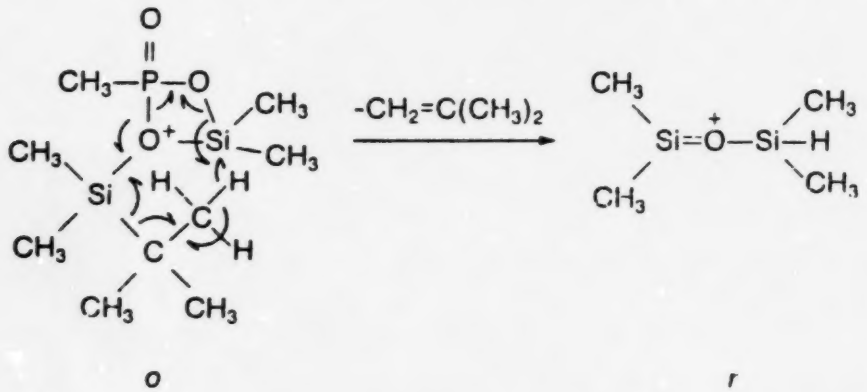
Another of the prominent ions found for the alkylphosphonic acid derivatives occurs at m/z 147. The origin of this ion can be attributed to the sequence shown in Scheme 9 for compound **4** analogous to the fragmentation pathway proposed for the disilyl derivatives of 1,2-diols and acids or their anions [15b,21k,24,26-28,30,31].

Observations of an abundant ion at m/z 133 have been made for other polysilyl derivatives [15b,28] leading to the suggestion of the



Scheme 9

empirical formula $[(CH_3)_3Si_2O_2]^+$. This formula predicts an isotope ratio of 134/133 of 13.6 whereas the observed ratios for compounds **4-7** are 13.3, 14.6, 14.7 and 14.9 respectively. Another suggestion seems plausible for this m/z, namely, $C_4H_{13}OSi_2$ with calculated isotope ratio of 14.6. Scheme 10 can be proposed starting with the $[M-57]^+$ ion *o* for

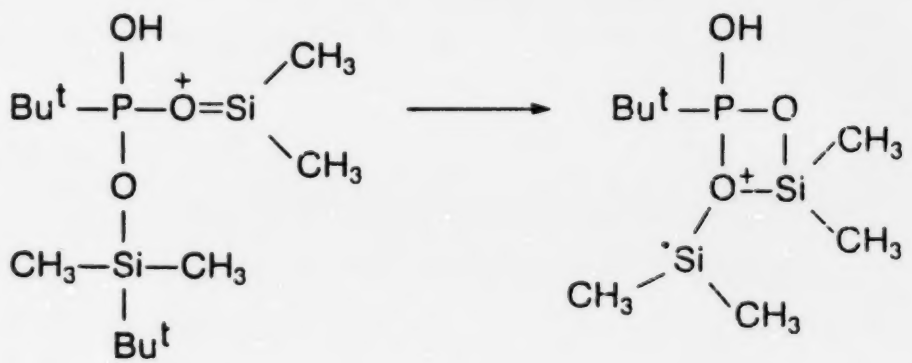


Scheme 10

compound 4. Further dissociation of ion *r* to form $[Si(CH_3)_2OH]^+$ (m/z 75) or $[Si(CH_3)_2]^+$ (m/z 58) could occur and abundant ions are found at both of these m/z. An examination by high resolution mass spectrometry should aid in verifying the identity of the proper empirical formula for m/z 133 and is now underway.

Other major ions with m/z less than 133 are in common with the spectra of the alkyl methylphosphonic acid derivatives and suggestions for their structure and modes of formation have already been suggested.

Two other minor series of ions deserve mention. In Table 2, the intensity of m/z 210 is included because of its relative abundance of 5.1% for compound 7. The negligible levels found for the alkyl methylphosphonic acid derivatives indicate that this ion is related to disilyl compounds. One possible ion fragmentation pathway which could occur in compound 7 is depicted in Scheme 11. The relative abundance



s *t*

Scheme 11

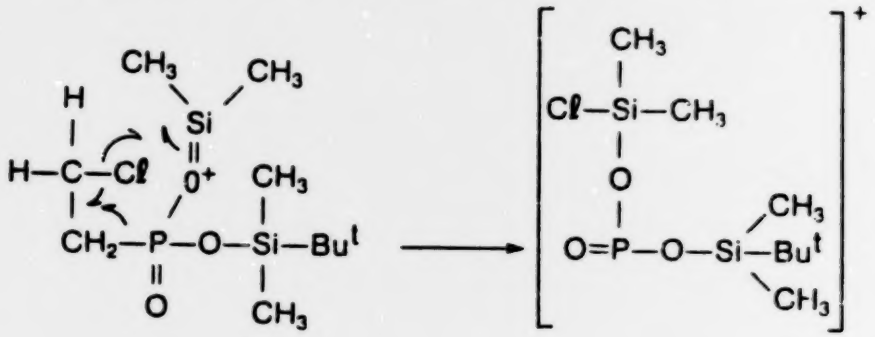
of m/z 253 is, in fact, 1.1%. Since there is an n-butyl chain attached to the phosphorus atom, subsequent fragmentation similar to that observed in hydrocarbons may occur with a loss of CH_3(m/z 238), C_2H_5 (m/z 224), C_3H_7 (m/z 210) or C_4H_9 (m/z 196) which have respective relative abundances of 0.3, 1.1, 5.1, and 7.1% although the m/z 196 peak is probably acquiring intensity from other pathways. In compound **6**, the relative abundances corresponding to ion *t* and losses of 15 and 29 u are 1.4, 1.3, and 2.7% respectively while for compound **5**, the relative abundances for ion *t* and loss of 15 u are 2.4 and 1.2%. Another series of ions which also appears to be associated with the disilyl compounds is that of m/z 253, 267, 281, and 295 for compounds **4**-**7** respectively. One possible fragmentation pathway which could satisfy the requirement would be an initial loss of a methyl group, which is observed, coupled with a hydrogen transfer and subsequent loss of isobutene in a step similar to that depicted in Scheme 7. Both of these proposals are speculative without the aid of high resolution measurements and further investigations.

3.3 2-Chloroethylphosphonic Acid Derivative (Compound 8)

On comparison of the t-BDMS derivatives of 2-chloroethylphosphonic acid (Ethephon) and ethylphosphonic acid, many similarities and a few significant differences are apparent. In the lower mass regions, the similarities are more numerous with such common peaks as m/z 57, 59, 73, 121, 133, 135, 147 and 195. Since these peaks have been proposed to result from silyl rearrangement products not involving the R-P(O)

segments, similarities between the spectra of the two compounds are consistent with the pathways and empirical formulae proposed earlier.

Although a detailed examination will not be carried out at this time, several observations should be noted. There is an abundant ion at m/z 287 or (M-85) and at m/z 289, the ratio of which indicates that the chlorine atom is still present. The loss of 85 u infers that a rearrangement has taken place. One possible structure for the ion at m/z 287 and its mechanism of formation from the $[M-57]^+$ ion is depicted in Scheme 12 although this mechanism does involve cleavage of the P-C bond. Evidence that chlorine atoms can migrate in silyl-derivatized

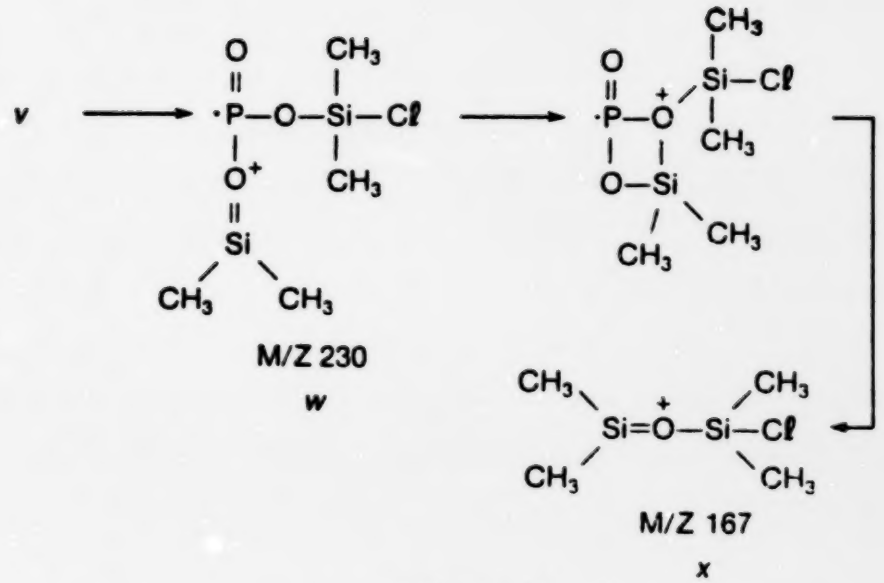


u *v*

Scheme 12

compounds has been observed previously [32]. Consistent with the suggestion of chlorine atom transfer is the presence of an ion at m/z 167 with its Cl^{37} isotope at m/z 169. In a step analogous to the formation of the ion at m/z 147, an ion at m/z 167 could be produced as depicted in Scheme 13.

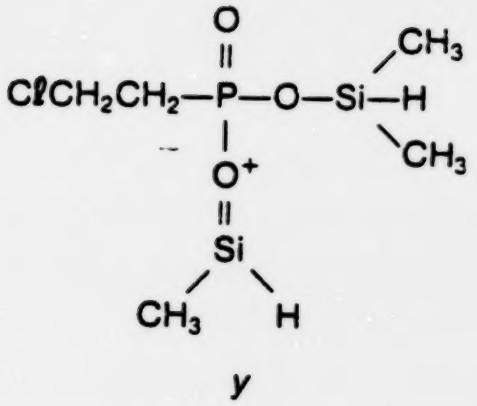
A peak at m/z 230 is, in fact, observed lending support to this pathway for formation of the ion at m/z 167. Furthermore, a peak at m/z 93 with a second peak at m/z 95 is observed consistent with subsequent



Scheme 13

silicon-oxygen cleavage in either ions *v* or *x*. As with other proposals for empirical formulae proposed in this paper, high resolution determination is necessary for final confirmation.

The peak at m/z 245 also contains chlorine as indicated by the abundance of the ion at m/z 247 (38% of the abundance of m/z 245) while the relatively high intensity of m/z 246 (13.4% of m/z 245) strongly suggests that both silicon atoms are still present. It is unlikely that a chlorine transfer similar to that proposed above for the m/z 287 ion (ion *v*) formation occurs in this case since the accompanying loss would be 99 u which, if both silicon atoms are retained, is not easily accounted for. A more likely structure is given in Figure 1. The isotope ratios for m + 1, m + 2 and m + 3 are calculated to be 16.1, 40.3



y

Figure 1

and 6% respectively whereas the observed ratios are 13.4, 38.4 and 4%. As noted in earlier spectra, the ion at m/z 59, which has a significant relative abundance of 5.5%, could result from subsequent silicon-oxygen bond cleavage.

Isotopic ratios of the abundance of the ions at m/z 216 and m/z 217 to that of m/z 215 indicate that the m/z 215 ion retains the chlorine atom as well as both silicon atoms. One empirical formula which generally satisfies these requirements is $C_3H_9O_3PSi_2Cl$. However verification of this empirical formula is necessary before further meaningful proposals can be made concerning the structure or the mechanism of its formation.

4.0 CONCLUSION

In general, the application of t-BDMS-derivatization to the analysis of alkyl methylphosphonic, alkylphosphonic and halogen-substituted alkylphosphonic acids represents a significant advance in that these compounds may now be routinely analyzed without the disadvantages attending the use of diazoalkanes. The gas chromatographic separation of the compounds investigated in this study is excellent and peak shape is good [22]. In addition, the reaction conditions appear to be mild and the products very stable [22]. The limited fragmentation resulting in significant proportions of the ion current residing in only a few ions makes the t-BDMS derivatives of this class of compounds ideal candidates for quantitation and detection by mass spectrometric multiple ion detection (MID). The sensitivity limits of this approach as well as Flame Photometric GC detection will be reported elsewhere [22].

In the area of chemical-disarmament verification, these derivatives should prove to be very useful since the derivatives of partially and completely hydrolysed nerve agents can readily be detected by monitoring two ions, one at m/z 153 for derivatized alkyl methyl-phosphonic acid and one for derivatized methylphosphonic acid at m/z 267. The clean chromatography presents a retention index which, when used with the MID, should permit easy and rapid screening of residues. In addition, the presence of methyl methylphosphonic acid and the number of free hydroxyl groups can unambiguously be identified in contrast to diazomethylation derivatization. The fragmentation and rearrangement pathways proposed in this paper, in particular for those ions which have

not been previously observed in other silyl derivatizations, require further investigation for their verification. High resolution measurement is underway toward that end.

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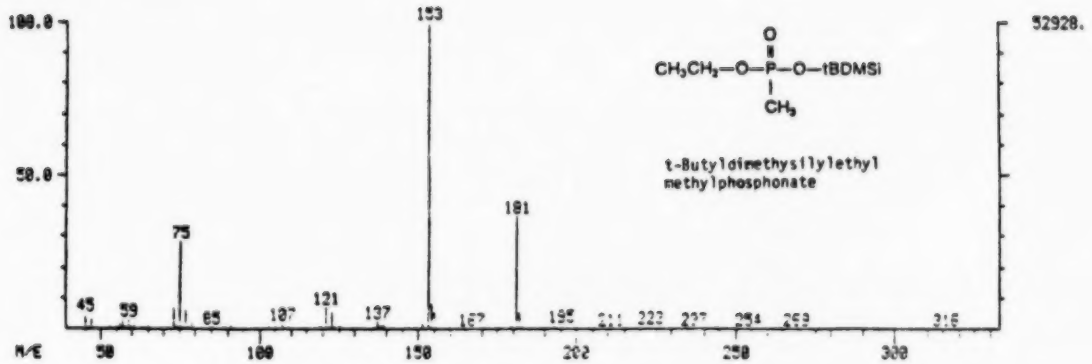
APPENDIX

MASS SPECTRA-COMPOUNDS 1-8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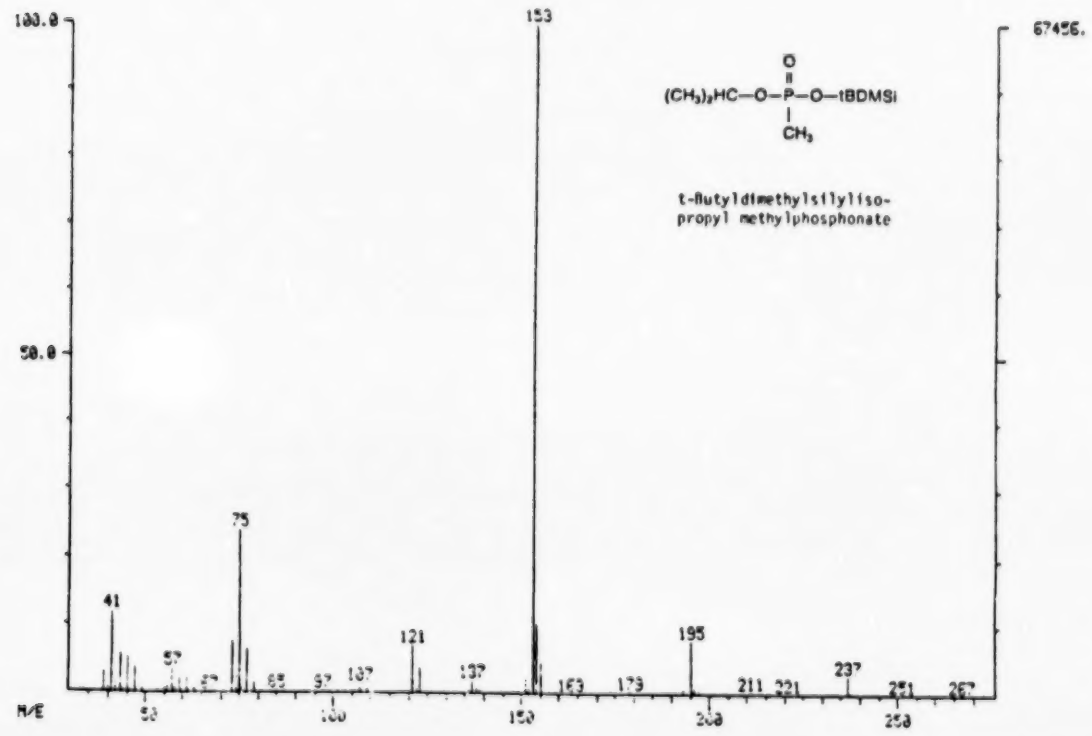
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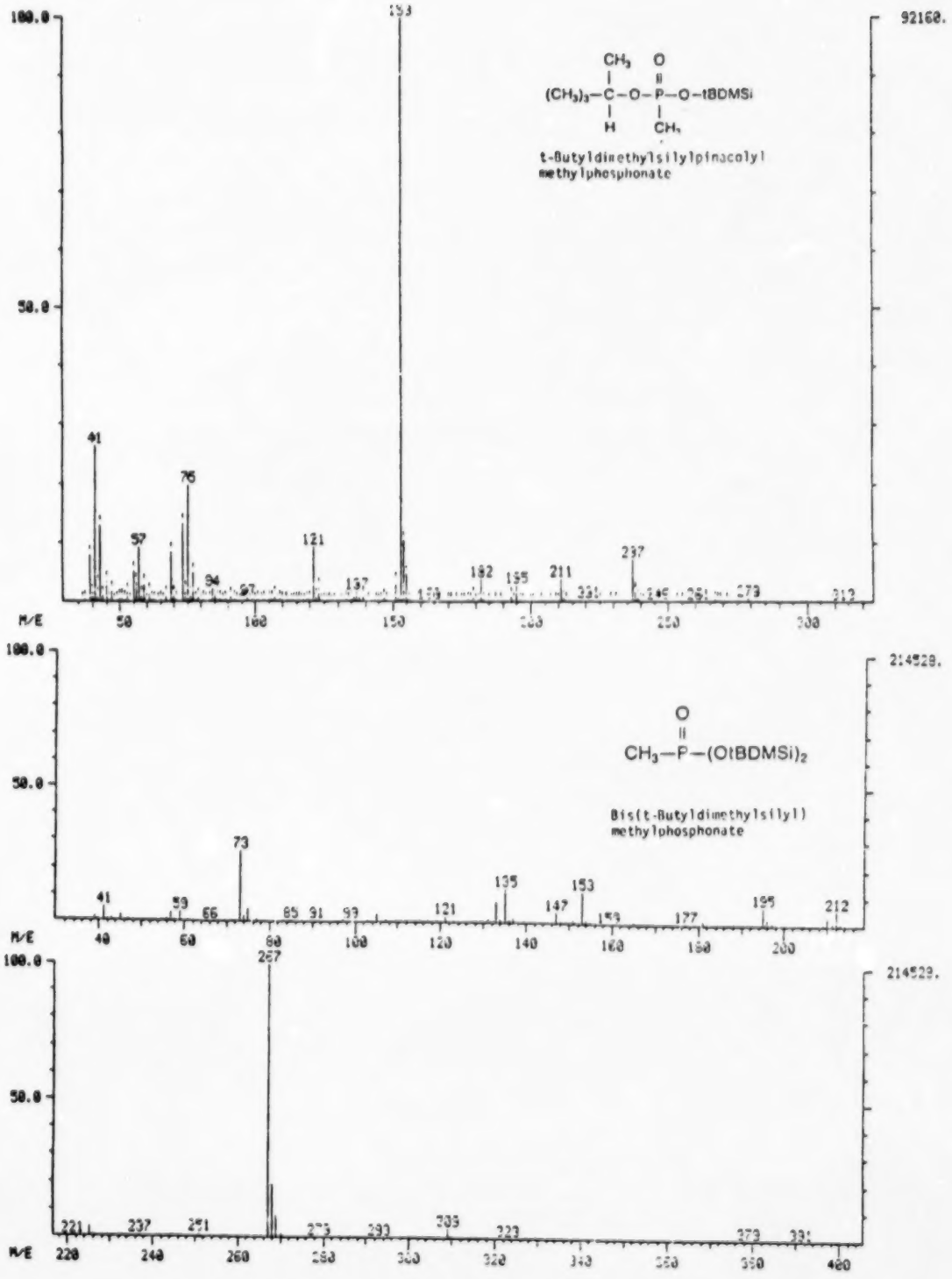
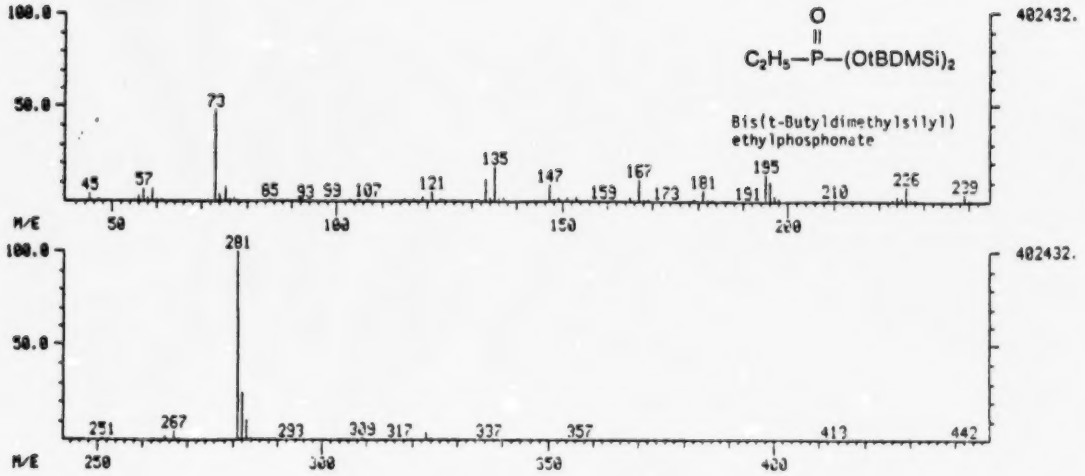

100.0
50.0
92160.
153
41
75
57
121
237
211
M/E
50
100
150
200
250
300
CH3 O
(CH3)3—C—O—P—O—tBDMSi
H CH3
t-Butyldimethylsilylpinacolyl
methylphosphonate
100.0
50.0
214528.
O
CH3—P—(OtBDMSi)2
Bis(t-Butyldimethylsilyl)
methylphosphonate
73
41
135
153
147
177
195
212
M/E
40
60
80
100
120
140
160
180
200
100.0
50.0
214529.
257
221
237
251
223
M/E
220
240
260
280
300
320
340
360
380
400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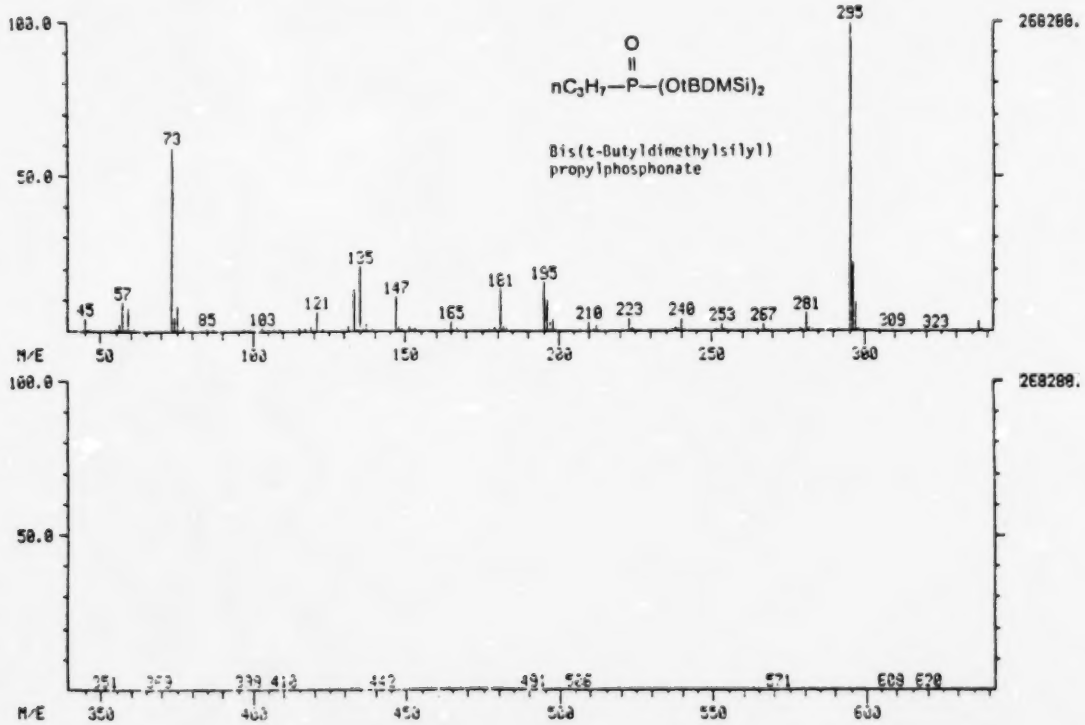
50.0
O
||
C2H5—P—(OtBDMSi)2
Bis(t-Butyldimethylsilyl)
ethylphosphonate
402432.
73
135
147
195
281
M/E
50
100
150
200
250
300
350
400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O
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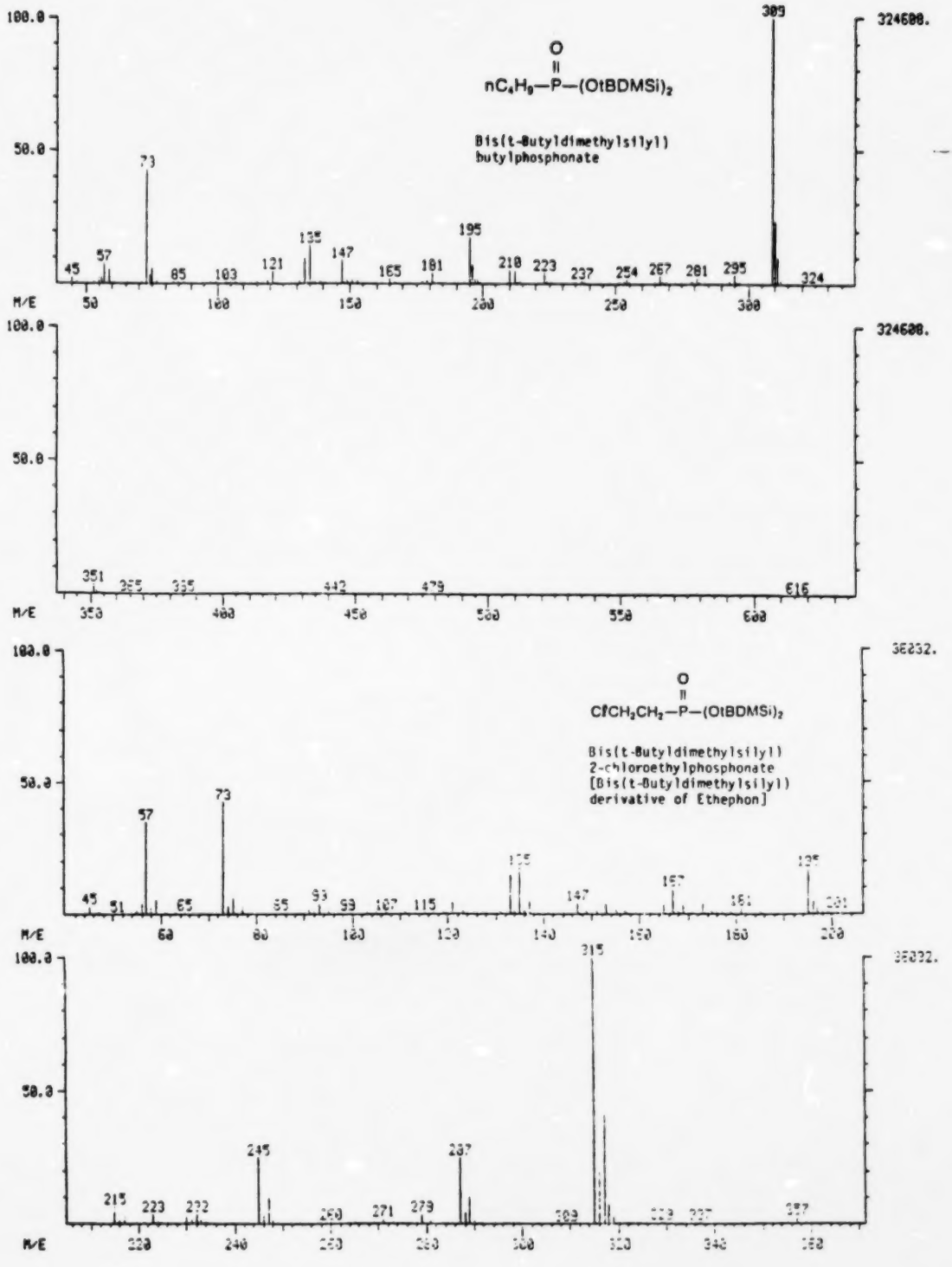
nC3H7—P—(OtBDMSi)2
Bis(t-Butyldimethylsilyl)
propylphosphonate
268288.
73
135
147
181
195
281
295
M/E
50
100
150
200
250
300
350
400
450
500
550
600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Bis(t-Butyldimethylsilyl)
butylphosphonate
73
57
45
85
103
121
135
147
165
181
195
210
223
237
254
267
281
295
309
324
M/E
50
100
150
200
250
300
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50.0
324600.
351
385
335
442
479
616
M/E
350
400
450
500
550
600
100.0
50.0
38232.
O
ClCH2CH2—P—(OtBDMSi)2
Bis(t-Butyldimethylsilyl)
2-chloroethylphosphonate
[Bis(t-Butyldimethylsilyl)
derivative of Ethephon]
57
73
45
51
65
85
93
99
107
115
135
147
167
181
195
201
M/E
60
80
100
120
140
150
160
200
100.0
50.0
38232.
315
245
287
215
223
232
260
271
279
303
329
337
357
M/E
220
240
260
280
300
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340
360

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13 ABSTRACT

(U) Electron impact mass spectra have been generated for t-butyldimethylsilyl-derivatives of several alkyl methylphosphonic, alkylphosphonic and halogen-substituted alkylphosphonic acids. In all cases, fragmentation is limited to a few abundant ions indicating that improved quantitation of organophosphonic acids, essential for verification of chemical arms agreements, will be possible by gas chromatograph/mass spectrometric means using these derivatives. Some fragmentation mechanisms are suggested to account for the major ions of the spectra.

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Phosphorus organic acid esters
Phosphorus organic compounds
Chemical warfare agents
Military chemical agents
Phosphonic acids
Phosphorus organic acids
Silicon organic compounds

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